Supporting information for:
Modeling Electron Transfer in Diffusive Multidimensional Electrochemical Systems

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Appendix A: Stencil details for 2D simulations

When simulating 2D voltammetry experiments using the diagonalized Fokker-Planck operator, one requires a high order of accuracy for approximating the second derivative calculation with respect to $\zeta$. To achieve convergent results using this approach, a higher order second derivative stencil was utilized. Specifically, we used a centered difference, 17-stencil, which is accurate to sixteenth order with respect to the grid spacing in $\zeta$, $\mathcal{O}(d\zeta^{16})$. For calculating the derivative at grid point $\zeta_i$ the stencil contains the points $[\zeta_i - 8d\zeta, \zeta_i + 8d\zeta]$, with weights calculated by elimination of lower order error terms using the Taylor expansions of $[\zeta_i - 8d\zeta, \zeta_i + 8d\zeta]$.$^1$ For the x-direction, we used a simple 3-stencil with points $[x_i - dx, x_i, x_i + dx]$ for points $x_i$.

Appendix B: The transition from a separable to a non-separable Hamiltonian

In figures 8 and 9 we plot results for the case that $\zeta_A(x) \approx \zeta_A^0$ at $x = 0$ and $\zeta_A(x) \approx \zeta_A^\infty$ for $x \neq 0$ (see equation 39). In practice, this choice of $\zeta_A(x)$ corresponds to choosing a sufficiently large value of $\sigma$ for the analytical expression, $\zeta_A(x) = (\zeta_A^0 - \zeta_A^\infty)e^{-\sigma x^2} + \zeta_A^\infty$. Thus, in this limit, the $x$ and $\zeta$ directions are far from separable: the reorganization energy (characterizing the shift of $\zeta$ as a function of charge states) depends critically and dramatically on the distance to the metal ($x$).

Now, that being such, one can increase separability by choosing a smaller value of $\sigma$ (see equation 39), so that the reorganization energy changes more slowly as a function of $x$. To that end, in figure S1 we plot (on the left) linear sweep voltammograms for different $\sigma$ values and (on the right) the well minimum position $\zeta_A$ as a function of the grid point in $x$, $x_i$. For small $\sigma$ values, where there is little difference between $\zeta_A(x)$ values at the first few grid points, we find that the 1D MH model and the full 2D model agree quantitatively. This
Figure S1: (left) Linear sweep voltammograms and (right) ζ_A positions as a function of x for different σ values in ζ_A(x) (see equation 39). ΔG_i = 0.816 V, ΔG_f = −0.816 V, ζ_A^0 = −6.35 Å (−12 a.u.), ζ_A^∞ = −5.29 Å (−10 a.u.), D = 5.5 · 10^{-4} cm^2/sec, ω = 1.03 · 10^{13} sec^{-1}, λ_0 = 31.8 kT, Γ = 1.40 · 10^9 cm/sec, and ν = 112 V/sec for each subplot. (a) & (d) σ = 0.0001 dx^2, (b) & (e) σ = 0.01 dx^2, (c) & (f) σ = 0.1 dx^2. For small σ values, where ζ_A depends slowly on x and motion in x and ζ is largely separable, we see quantitative agreement between the 1D MH and 2D models. However, for large σ values, where there is no separability, the 1D MH and 2D models do not agree.

results confirms our intuition: the full 2D dynamics can be reduced to 1D when the x and ζ directions are close to separable.
Appendix C: Implementation of 1D BV and Nernstian boundary conditions

For Nernstian dynamics (equation 4) and Butler-Volmer dynamics (equations 5 and 6) there are two unknowns \((c_A(x = 0)\) and \(c_B(x = 0)\)) at the surface, but only one equation. As such, one additional equation is needed. To that end, it is standard\(^{S2}\) to use the additional constraint that the flux of species A and B are equal and opposite at the boundary,

\[
J_A|_{x=0} = D_A^x \frac{\partial c_A}{\partial x}|_{x=0} = k_f c_A|_{x=0} - k_b c_B|_{x=0} \tag{1a}
\]

\[
J_B|_{x=0} = D_B^x \frac{\partial c_B}{\partial x}|_{x=0} = -k_f c_A|_{x=0} + k_b c_B|_{x=0}. \tag{1b}
\]

Using a 2 stencil with a forward difference approximation for the spatial derivatives \((\frac{\partial c_i}{\partial x} = \frac{c_{i,1} - c_{i,0}}{dx}\) for species \(i\)), one can arrive at the following boundary values for Nernstian dynamics:

\[
c_{A,0} = \frac{c_{B,1} + \frac{D_A^x}{D_B^x} c_{A,1}}{\frac{D_A^x}{D_B^x} + e^{-\beta \Delta G}} \tag{2a}
\]

\[
c_{B,0} = c_{A,0} e^{-\beta \Delta G}, \tag{2b}
\]

and for Butler-Volmer dynamics:

\[
c_{A,0} = \frac{c_{B,1} k_b dx + D_A^x c_{A,1} (1 + \frac{k_b dx}{D_B^x})}{D_A^x + dx (k_f + \frac{D_A^x}{D_B^x} k_b)} \tag{3a}
\]

\[
c_{B,0} = c_{B,1} + \frac{D_A^x}{D_B^x} (c_{A,1} - c_{A,0}). \tag{3b}
\]

References